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Stability Evaluation of Sulfur Dioxide, Nitric Oxide and Carbon Monoxide Gases in Cylinders

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STABILITY EVALUATION OF SULFUR DIOXIDE, NITRIC OXIDE AND CARBON MONOXIDE GASES IN CYLINDERS

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16. ABSTRACT

The US EPA recommends in their EPA Traceability Protocol 1 and 2 that reactive gases be reanalyzed every six months. The purpose of this study was to assess the stability of selected reactive gases as a function of time to determine the feasibility of extending the recertification period. The reactive gases in this study were contained in aluminum and steel cylinders and included: carbon monoxide in air (CO/Air); carbon monoxide in nitrogen (CO/N_2); nitric oxide in nitrogen (NO/N_2); and sulfur dioxide in nitrogen (SO_2/N_2).

Stability information extending over time periods of one year or longer was solicited from federal, state, and local agencies; the State and Local Air Monitoring System (SLAMS) Ambient Air Audit Centers; and selected specialty gas manufacturers. Stability data were received for a total of 316 compressed gas cylinders. There were 300 aluminum cylinders consisting of: 37 CO/air, 86 CO/N_2, 103 NO/N_2, and 74 SO_2/N_2 cylinders. Sixteen of the cylinders were steel. Time intervals (between initial and final analyses) covered by the stability data in this report ranged from 10 to 58 months with the average time interval being well over 12 months.

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CONTENTS

Section		Page
1	SUMMARY	1
2	INTRODUCTION	5
3	DATA COLLECTION	7
4	STABILITY ASSESSMENT PROCEDURES, RESULTS, AND DISCUSSION	9
	Procedures	9
	Results	10
	Carbon Monoxide in Air Contained In Aluminum Cylinders	10
	Carbon Monoxide in Nitrogen Contained In Aluminum Cylinders	14
	Nitric Oxide in Nitrogen Contained In Aluminum Cylinders	20
	Sulfur Dioxide in Nitrogen Contained In Aluminum Cylinders	28
	Carbon Monoxide in Air Contained In Steel Cylinders	36
	Carbon Monoxide in Nitrogen Contained In Steel Cylinders	38
	Discussion	41
5	CONCLUSIONS AND RECOMMENDATIONS	44
6	REFERENCES	46

TABLES

Number		Page
1	Summary of Reactive Gases Contained in Aluminum Cylinders	3
2	Summary of Reactive Gases Contained in Steel Cylinders	4
3	Sources of Reactive Gas Stability Data	8
4	Stability Data for CO/Air in Aluminum Cylinders	11
5	Stability Data for CO/Nitrogen in Aluminum Cylinders	15
6	Stability Data for NO/Nitrogen in Aluminum Cylinders	21
7	Stability Data for SO_2/Nitrogen in Aluminum Cylinders	29
8	Stability Data for CO Contained in Steel Cylinders	37
9	Average Percent Change and Probability Limits of Reactive Gases Contained in Aluminum Cylinders for Eighteen Months	42
10	Percent Change and Probability Limits of Reactive Gases Contained in Steel Cylinders for Eighteen Months	42

SECTION 1

SUMMARY

The Environmental Protection Agency (EPA) recommends that reactive gases be reanalyzed every six months (Ref. 1). The purpose of this task was to assess the stability of selected reactive gases as a function of time to determine the feasibility of extending the recertification period. The reactive gases in this study were contained in aluminum and steel cylinders and included: carbon monoxide in air (CO/Air); carbon monoxide in nitrogen (CO/N_2); nitric oxide in nitrogen (NO/N_2); and sulfur dioxide in nitrogen (SO_2/N_2).

Stability information extending over time periods of one year or longer was solicited from federal, state, and local agencies; the State and Local Air Monitoring System (SLAMS) Ambient Air Audit Centers, maintained under contract to the EPA's Environmental Monitoring Systems Laboratory in the Research Triangle Park (EMSL-RTP); and selected specialty gas manufacturers. Stability data were received for a total of 316 compressed gas cylinders. There were 300 aluminum cylinders consisting of: 37 CO/air, 86 CO/N_2, 103 NO/N_2, and 74 SO_2/N_2 cylinders. Sixteen of the cylinders were steel. Time intervals (between initial and final analyses) covered by the stability data in this report ranged from 10 to 58 months with the average time interval being well over 12 months.

Stability data were subdivided into pollutant category (CO/Air, CO/N_2, NO/N_2, and SO_2/N_2), pollutant/balance gas concentration ranges, and cylinder construction (aluminum or steel). Stability of the reactive gases was assessed by calculating a linear regression equation of concentration versus time in months from the initial analysis for each cylinder. The slope of the resultant linear regression equation was in units of ppm change per month. When the slope was multiplied by a number of months, the product equaled a change in pollutant concentration (ppm) for that specific number of months.

The average percent change of a median concentration within each pollutant category and concentration range was calculated for time

periods of 6, 12, 18, and 24 months in Table 1 for aluminum cylinders. All the reactive gases contained in aluminum cylinders evaluated indicated average changes of 1 percent or less over an 18 month period.

The percent change of a median concentration within each pollutant category and concentration range was calculated for 6, 12, 18, and 24 months in Table 2 for steel cylinders. The CO/air and CO/N_2 gases contained in steel cylinders indicated a greater change in concentration over time than they did in aluminum cylinders. However, this observation for CO in steel cylinders was based on a considerably smaller data set.

Using a stability criterion of an average change of ± 1 percent or less for a pollutant category as acceptable, and an average change greater than ± 1 percent as unacceptable, the following were recommended:

- o That the present requirement for reanalysis of reactive gases every six months be extended to eighteen months for the following:
  - Carbon monoxide in air contained in aluminum cylinders at concentrations between 5 ppm and 45 ppm. NOTE: To ensure uncertainties of less than 10 percent for measured concentrations near 5 ppm, it may be necessary to use the average of two analyses.
  - Carbon monoxide in nitrogen contained in aluminum cylinders at concentrations between 5 ppm and 5,000 ppm. NOTE: To ensure uncertainties of less than 10 percent for measured concentrations near 5 ppm, it may be necessary to use the average of two analyses.
  - Nitric oxide in nitrogen contained in aluminum cylinders at concentrations between 10 ppm and 150 ppm.
  - Sulfur dioxide in nitrogen contained in aluminum cylinders at concentrations between 8 ppm and 375 ppm.
- o That the present requirement for reanalysis of reactive gases every six months remain unchanged for the following:
  - Carbon monoxide in air contained in steel cylinders.
  - Carbon monoxide in nitrogen contained in steel cylinders.

Current recertification requirements should remain unchanged for reactive gases and cylinder types not considered in this report.

TABLE 1. SUMMARY OF REACTIVE GASES CONTAINED IN ALUMINUM CYLINDERS[a,b]

Pollutant Category	Number of Standards	Concentration Range (ppm)	Median, X Concentration (ppm)	Slope, m (ppm/month)		Average Percent Change, $\bar{P}$				s_p (18 mo) (%)
				$\bar{m}$	s_m	6 mo	12 mo	18 mo	24 mo	
CO/Air	10	5-11	7	-0.004	0.013	-0.3	-0.7	-1.0	-1.4	3.3
CO/Air	22	17-45	30	0.000	0.017	0.0	0.0	0.0	0.0	1.0
CO/N_2	16	5-15	10	+0.001	0.010	+0.0	+0.1	+0.2	+0.2	1.8
CO/N_2	17	19-46	30	+0.006	0.018	+0.1	+0.2	+0.4	+0.5	1.1
CO/N_2	16	100-1000	500	-0.112	0.268	-0.1	-0.3	-0.4	-0.5	1.0
CO/N_2	26	2500-5000	3750	+0.009	4.922	0.0	0.0	0.0	0.0	2.4
NO/N_2	7	10-22	16	-0.003	0.014	-0.1	-0.2	-0.3	-0.5	1.6
NO/N_2	25	43-55	49	-0.025	0.070	-0.3	-0.6	-0.9	-1.2	2.6
NO/N_2	71	80-113	97	-0.009	0.112	-0.1	-0.1	-0.2	-0.2	2.1
SO_2/N_2	10	9-22	15	-0.003	0.020	-0.1	-0.2	-0.4	-0.5	2.4
SO_2/N_2	21	45-56	51	+0.007	0.070	0.0	+0.2	+0.2	+0.3	2.5
SO_2/N_2	33	78-110	94	-0.039	0.115	-0.2	-0.5	-0.7	-1.0	2.2
SO_2/N_2	10	152-375	264	+0.061	0.103	+0.1	+0.3	+0.4	+0.6	0.7

[a] See Section 4 for further explanation.

[b] Definition of terms

X = Median concentration of a concentration range or pollutant category, ppm.

$\bar{m}$ = Average slope for all cylinders in a concentration range (i.e., a pollutant category), ppm change/month.

s_m = Standard deviation of the slope calculated for each concentration range, ppm change/month.

$\bar{P} = 100(\bar{m})(T)/X$, average percent change for a nominal concentration over a specified time period, percent.

$s_p = 100(s_m)(T)/X$, standard deviation of percent change at the nominal concentration, over time period T, percent.

TABLE 2. SUMMARY OF REACTIVE GASES CONTAINED IN STEEL CYLINDERS[a,b]

Pollutant Category	Number of Standards	Concentration Range (ppm)	Median, X Concentration (ppm)	Slope, m (ppm/month)		Average Percent Change, $\bar{P}$				s_p (18 mo)
				$\bar{m}$	s_m	6 mo	12 mo	18 mo	24 mo	
CO/Air	5	9-11	10	-0.028	0.020	-1.7	-3.4	-5.0	-6.7	3.6
CO/N_2	9	19-43	31	-0.032	0.029	-0.6	-1.2	-1.9	-2.5	1.7
CO/N_2	2	1000	1000	0.153	0.095	-0.1	-0.2	-0.3	-0.4	0.2

[a] See Section 4 for further explanation.

[b] Definition of terms

X = Median concentration of a concentration range or pollutant category, ppm.

$\bar{m}$ = Average slope for all cylinders in a concentration range (i.e., a pollutant category), ppm change/month.

s_m = Standard deviation of the slope calculated for each concentration range, ppm change/month.

$\bar{P} = 100(\bar{m})(T)/X$, average percent change for a nominal concentration over a specified time period, percent.

$s_p = 100(s_m)(T)/X$, standard deviation of percent change at the nominal concentration, over time period T, percent.

SECTION 2

INTRODUCTION

A model used to estimate the optimum time interval for recertification of pollutant concentration in a cylinder should include the following terms:

- the indicated stability of that pollutant at a specified concentration and in a particular cylinder type as a function of time;
- the precision, and potential for bias, of the certification process;
- the costs associated with recertification; and
- the costs associated with generating environmental data of poor quality (when used as a calibration or audit standard) and the cost associated with rejecting good quality data as bad (when used as an audit standard for QC or QA purposes).

Due to limited resources this assessment of an acceptable recertification time period was limited to consideration of the first two items listed above. First, the stability of pollutants in cylinders was assessed using results of analyses over time by computing a linear regression equation of measured concentration versus time in months since the initial analysis for each pollutant cylinder. The slope of the equation represents the change in concentration in ppm per month. Results for all the pollutant cylinders in a specific category were combined and the average percent change per month and the pooled standard deviation of the percent changes were used to construct probability intervals for percent change in concentration for individual pollutant cylinders in that category. The difference between the average slope and the ideal slope of 0.000 ppm change/month was checked both for statistical significance in general and for practical significance for specific time intervals of interest.

The pooled standard deviation for analysis results for a pollutant cylinder category was used to estimate the range of error that can be expected for the pollutant concentration, based on one analysis.

Reactive gas stability data contained in this report were evaluated to determine if the reanalysis period stated in Section 1.2.5 of EPA Protocol No. 2 (Ref. 1) could be extended beyond six months for CO, NO, and SO_2 reactive gases contained in aluminum and steel cylinders.

Traceability Protocol No. 2 provides procedures for establishing the true concentration of reactive gases using National Bureau of Standards (NBS) gaseous Standard Reference Materials (SRMs) or EPA/NBS-approved commercial Certified Reference Materials (CRMs), as stated in EPA Regulations (Ref. 2). "Traceable" means that a standard has been compared and certified, either directly or via not more than one intermediate standard, to an SRM or CRM.

The reactive gas stability evaluation was initiated by soliciting existing stability data from federal, state, and local agencies; the State and Local Air Monitoring Systems (SLAMS) Ambient Air Audit Centers, maintained under contract to the EPA's Environmental Monitoring Systems Laboratory in the Research Triangle Park (EMSL-RTP); and selected specialty gas manufacturers. Also contained in the analysis were reactive gas stability data provided by the Quality Assurance Division of EMSL-RTP. Stability data were received for a total of 300 reactive gases in aluminum and steel cylinders.

Section 3 discusses data collection procedures and categorizes the sources of the stability data used in this evaluation. Section 4 discusses data analysis techniques and Section 5 contains conclusions and recommendations.

SECTION 3
DATA COLLECTION

Reactive gas stability data were solicited by letter from RTI to federal, state, and local agencies, SLAMS Ambient Air Audit Centers, and selected specialty gas manufacturers. Also included in these data are 112 reactive gas cylinders analyzed by the EPA-EMSL/QAD standards laboratory. Data were requested on reactive gas cylinders that had been analyzed over a time period of twelve months or longer. The requested information included a brief description of the analysis procedure, analyzed concentrations, time elapsed between analyses, and cylinder identification information (cylinder number, size, and construction material).

Table 3 has been included to show the distribution across sources of the stability data. This table also indicates methods of analysis used by the sources of stability data.

It must be emphasized here that the data collected for this project may not be representative of the typical results achieved by laboratories across the country for these types of analyses. For example, results obtained for specific pollutant cylinders showing dramatic changes with time may have been excluded from the data sets. The data sets received for this project should, perhaps, not be used to estimate the probability of experiencing a large bias in the certification process, as would occur from a calculation mistake or a poor analysis. Also, the precision estimated from these data may be better than is routinely realized in many organizations.

TABLE 3. SOURCES OF REACTIVE GAS STABILITY DATA

Source Code[a]	Number of Reactive Gases					Percent of Total Data
	CO/Air	CO/N_2	NO/N_2	SO_2/N_2	Total	
A	1	34	37	40	112	37
B	16	37	39	20	112	37
C	10	15	6	5	36	12
D	2	0	8	7	17	6
E	8	0	13	3	24	8
TOTAL	37	86	103	75	301	100

[a] A: Analyzed by the EPA-EMSL/QAD standards laboratory using source level analyzers; carbon monoxide cylinders were analyzed using an ambient level analyzer.

B: Analyzed by SLAMS Ambient Air Audit Centers using source level analyzers and Protocol No. 2.

C: Analyzed by federal, state or local monitoring agencies using source level analyzers and Protocol No. 2.

D: Analyzed by federal, state or local monitoring agencies using dilution devices and ambient level analyzers.

E: Analyzed by commercial gas manufacturers.

SECTION 4

STABILITY ASSESSMENT PROCEDURES, RESULTS, AND DISCUSSION

PROCEDURES

Stability data were received for 37 CO/Air, 86 CO/N_2, 103 NO/N_2, and 75 SO_2/N_2 for a total of 301 compressed gases. The analysis period covered by the reported data ranged from 10 to 58 months. Each pollutant/balance gas category (CO/Air, CO/N_2, NO/N_2, SO_2/N_2) was divided into concentration ranges and cylinder construction (aluminum or steel). The concentration ranges were selected according to the concentration distribution of the stability data in order to more accurately evaluate a percent change for a specific concentration.

Stability of the reactive gases was assessed by calculating a linear regression equation of concentration versus time in months from the initial analysis for each cylinder. The slope of the resultant regression equation was in units of ppm change per month. When the slope was multiplied by a number of months, the product equaled a change in pollutant concentration (ppm) for that specific number of months. Also calculated for each pollutant category were the average slope, the standard deviation of the slopes, and, based upon a median concentration in each range, an average percent change for 6, 12, 18, and 24 months, and the standard deviation of the percent change for an 18 month period (see Tables 1 and 2 of Section 1).

Within a specific pollutant category, the average percent change ($\bar{P}$) over the 6, 12, 18, and 24 month periods was used as a measure of the stability of the pollutant category. Two times the standard deviation of the percent change (s_p) represented the approximate 95 percent probability limits for the percent change of individual pollutant cylinders in the category.

The following variables and formulas were used to calculate the stability of the reactive gases:

X = Median concentration of a concentration range or pollutant category, ppm.

$\bar{m}$ = Average slope for all cylinders in a concentration range ppm change/month.

s_m = Standard deviation of the slope calculated for each concentration range, ppm change/month.

T = Time, months

$\bar{P} = 100(\bar{m})(T)/X$, average percent change for a median concentration over a specified time period, percent.

$s_p = 100(s_m)(T)/X$, standard deviation of percent change at the median concentration, over time period T, percent.

$\pm 2\ s_p$ = 95% probability limits for the percent change of a reactive gas concentration, percent.

s_y = standard deviation of the measured concentrations for a specific cylinder, ppm.

$s_{yp} = [((n_1-1)\ s_{y1}^2 + \cdots + (n_k-1)\ s_{yk}^2)/(n_1 + \cdots + n_k-k)]^{1/2}$, pooled standard deviation of the measured concentrations across cylinders within a pollutant cylinder category, ppm.

RESULTS

Carbon Monoxide In Air Contained In Aluminum Cylinders

Stability data from thirty-seven aluminum cylinders containing carbon monoxide with a balance gas of air were analyzed. This stability data (cylinder number, date of initial analysis, initial concentration, method of initial analysis, time in months (T) since the initial analysis, and the analyzed concentration in ppm are contained in Table 4. Also contained in this table are the linear regression coefficients: slope (m), intercept (b) calculated from the analyzed concentrations versus time in months since the initial analysis, and the standard deviation (s_y) of the y axis values (measured CO concentrations). The data were subdivided into concentration ranges and analyzed according to a median concentration for the range. The concentration ranges were selected according to what appeared to be natural gaps in the concentration distribution of the data. Also, using relatively small concentration intervals allows one to assume constant

TABLE 4. STABILITY DATA FOR CO/AIR IN ALUMINUM CYLINDERS

ANALYSIS NO.	INITIAL ANALYSIS			SUBSEQUENT ANALYSIS[a]														
Cylinder No.	Date	Conc. (ppm)	Source[b]	Time T (months)	Conc. (ppm)	Time T (months)	Conc. (ppm)	Time T (months)	Conc. (ppm)	Time T (months)	Conc. (ppm)	Time T (months)	Conc. (ppm)	Time T (months)	Conc. (ppm)		m	b	s_y
BAL695-8	05-13-80	5.1	C	10	5.6	18	5.4										+0.018	5.20	0.25
BAL1180-9	01-24-80	5.6	B	9	5.6	19	5.4	40	5.5								-0.003	5.58	0.10
CAL6857-1	05-01-81	9.2	E	4	8.7	10	9.0	16	9.2	19	9.6	24	9.2				+0.018	8.93	0.29
CC3384-11	05-01-81	9.7	E	17	9.7												0.000	9.70	0.00
BAL1193-10	01-24-80	10.1	B	9	10.1	19	10.0	49	10.0								-0.003	10.10	0.06
AAL1053-5	11-04-80	10.6	B	10	10.0	23	10.3										-0.011	10.42	0.30
AAL420-6	11-04-80	10.6	B	10	10.1	23	10.3										-0.012	10.46	0.25
AAL1508-3	11-04-80	10.7	B	10	10.1	23	10.3										-0.016	10.54	0.31
AAL1710-4	11-04-80	10.7	B	10	10.2	23	10.3										-0.016	10.58	0.27
AAL459-7	11-04-80	10.7	B	10	10.1	23	10.3										-0.016	10.54	0.31
Summary Statistics: $\bar{m}$ = -0.004 ppm change/month; s_m = 0.013 ppm change/month; s_{yp} = 0.24 ppm																			
CC10574-32	09-01-80	17.9	E	8	18.0	25	17.9										-0.001	17.94	0.06
CC15074-19	05-01-81	18.0	E	17	17.9												-0.006	18.00	0.07
BAL1187-27	05-13-80	18.1	C	10	18.5	18	18.3										+0.012	18.19	0.20
CC4222-18	12-01-81	18.2	E	10	18.3												+0.010	18.20	0.07
CAL6997-16	05-01-81	18.9	E	4	19.2	10	18.8	16	19.4	19	19.9	24	19.0				+0.018	18.98	0.41
BAL1172-28	01-24-80	19.6	B	9	19.6	19	19.4	40	19.4								-0.006	19.60	0.12
SGCC27593-12	01-13-82	20.1	C	2	20.2	5	20.1	8	20.2	14	20.6	16	20.6				+0.034	20.05	0.24
BAL1190-29	01-24-80	29.6	B	9	29.7	19	29.4	40	29.7								+0.001	29.58	0.14
SGCC27603-53	01-13-82	29.0	C	2	29.0	5	29.1	8	29.0	14	29.3	16	29.4				+0.025	28.95	0.17
SGCC27774-13	01-13-82	40.2	C	2	40.4	5	40.4	8	40.3	14	40.4	16	40.6				+0.015	40.27	0.13
AAL2644-21	11-04-80	40.6	B	10	40.4	23	40.5										-0.004	40.54	0.10
AAL785-23	11-04-80	40.8	B	10	40.5	23	40.6										-0.008	40.72	0.15
AAL1707-25	11-04-80	40.8	B	10	40.6	23	40.7										-0.004	40.74	0.10
AAL4338-22	11-04-80	40.9	B	10	40.6	23	40.7										-0.008	40.82	0.15
AAL1990-24	11-04-80	41.2	B	10	40.9	23	41.0										-0.008	41.12	0.15
SGAL3235-14	01-29-82	41.8	D	10	41.7												-0.010	41.80	0.07
CC15150-31	09-01-80	41.9	E	8	41.8	25	41.7										-0.008	41.88	0.10
BAL1001-26	05-13-80	42.8	C	10	42.8	18	42.6										-0.011	42.83	0.12
BAL1181-17	05-01-81	43.1	E	4	43.2	10	42.2	16	43.3	19	43.7	24	43.5				+0.026	42.86	0.52
SGAL639-15	02-03-82	43.8	D	11	43.8												0.000	43.80	0.00
BAL1171-30	01-24-80	44.9	B	9	45.1	19	44.2										-0.038	45.09	0.47
AAL5920-20	06-11-81	45.1	B	9	45.1	19	44.7										-0.021	45.17	0.23
Summary Statistics: $\bar{m}$ = 0.000 ppm change/month; s_m = 0.017 ppm change/month; s_{yp} = 0.33 ppm																			

[a] T = Time in months since the initial analysis

[b] See Table 3

variances in the analysis. The CO/air data were divided into two concentration ranges, 5 to 11 and 17 to 45 ppm.

Concentration Range 5 to 11 ppm--

For CO/air in aluminum cylinders, there were 10 cylinders with measured concentrations ranging from 5 to 11 ppm (see Table 4). One of the cylinders was analyzed twice over a 17 month period, six were analyzed three times each over 18 to 23 month periods, two were analyzed four times each over a 40 month period, and one was analyzed six times over a 24 month period.

The 10 calculated regression equation slopes included seven negative, two positive and one zero values. The average slope was $\bar{m}$ = -0.004 ppm change/month and the standard deviation of the slopes about that average was s_m = 0.013 ppm change/month (see summary statistics in Table 4). Using the Student's t-test to test the hypothesis that the true mean slope was zero yielded:

$$t = \frac{\bar{m} - 0}{s_m/\sqrt{k}} = \frac{-0.004}{0.013/\sqrt{10}} = 0.973$$

Comparing the calculated t value to tabulated values for 9 degrees of freedom indicated that average slopes of 0.004 ppm change/month or larger could be expected to occur more than 20 percent of the time due to chance causes alone. Thus, there was no reason to reject the hypothesis that the mean slope was zero. An approximate 95 percent probability interval for slopes in this category was $\bar{m} \pm 2\ s_m$ = -0.004 $\pm$ 0.026 ppm change/month. For an 18 month period, for example, the 95 percent probability interval for change in concentration based on the distribution of the slopes was -0.072 $\pm$ 0.468 ppm (-0.54 to +0.40 ppm). Thus for a concentration value of 5 ppm the interval expressed as a percent is -11 percent to +8 percent.

The precision of analysis as estimated by the pooled standard deviation of the measured concentrations was s_{yp} = 0.24 ppm (see Table 4). The approximate 95 percent probability interval for the uncertainty (excluding bias) of a CO/air concentration estimated by one analysis was $\pm 2\ s_{yp}$ = 0.48 ppm or $\pm$10 percent at a concentration of 5 ppm.

Based on the above results it is concluded that:

- o 5 to 11 ppm CO/air in aluminum cylinders is stable over time periods greater than 18 months as evidenced by the average slope.

- o the precision of analysis at 5 ppm CO/air indicates the need for two independent Protocol No. 2 analyses in order to ensure errors of less than 10 percent.

- o the precision of analysis at 10 ppm CO/air indicates that repeated Protocol No. 2 analyses over an 18 month period are not necessary.

Concentration Range 17 to 45 ppm--

For CO/air in aluminum cylinders, there were 22 cylinders with measured concentrations ranging from 17 to 45 ppm (see Table 4). Four of the cylinders were analyzed twice each over 10 to 17 month periods, 11 were analyzed three times each over 10 to 25 month periods, two were analyzed four times over 40 month periods and five were analyzed six times over 16 to 24 month periods.

The calculated regression equation slopes include thirteen negative, eight positive and one zero values. The average slope was $\bar{m}$ = -0.000 ppm change/month and the standard deviation of the slopes about the average was s_m = 0.017 ppm change/month (see summary statistics in Table 4. Based on $\bar{m}$ = 0.000 ppm change/month there was no reason to reject the hypothesis that the true mean slope was zero. An approximate 95 percent probability interval for slopes in this category is $\bar{m} \pm 2\ s_m$ = 0.000 $\pm$ 0.034 ppm change/month. For an 18 month period, for example, the 95 percent probability interval for change in concentration based on the distribution of the slopes was 0.000 $\pm$ 0.612 ppm (-0.61 to +0.61 ppm) and for the median concentration value of 30 ppm the probability interval expressed as a percent was -2.0 percent to +2.0 percent.

The precision of analysis as estimated by the pooled standard deviation of the measured concentration was s_{yp} = 0.33 ppm (see Table 4). The approximate 95 percent probability interval for the uncertainty (excluding bias) of a CO/air concentration estimated by one analysis is $\pm 2\ s_{yp}$ = 0.66 ppm or $\pm$2.2 percent at the median concentration of 30 ppm.

Based on the above results it was concluded that CO/air in aluminum cylinders ranging in concentration from 17 to 45 ppm are stable

over time periods greater than 18 months, and the precision of analysis indicates that multiple Protocol No. 2 analyses over that time period are not necessary.

Carbon Monoxide In Nitrogen Contained In Aluminum Cylinders

Stability data from 75 aluminum cylinders containing carbon monoxide with a balance gas of nitrogen were analyzed. This stability data, cylinder number, date of initial analysis, initial concentration, method of initial analysis, time (T) in months since the initial analysis and the analyzed concentrations in ppm are contained in Table 5. Also contained in this table are the linear regression constants, slope (m) and intercept (b), calculated from the analyzed concentrations versus months since initial analysis and the standard deviation (s_y) of the y axis values (carbon monoxide concentrations). The data were subdivided into concentration ranges and analyzed according to a median concentration. The concentration ranges were selected according to what appeared to be natural gaps in the concentration distribution of the data. Also, using relatively small concentration intervals allows one to assume equal variances in the analysis. These data were divided into four concentration ranges, 5 to 15, 19 to 46, 100 to 1000 and 2500 to 5000 ppm.

Concentration Range 5 to 15 ppm--

For CO/Nitrogen in aluminum cylinders, 5 to 15 ppm, there were 16 cylinders with concentrations ranging from 5.6 to 15.2 ppm (see Table 5). Twelve of the cylinders were analyzed twice, over time periods ranging from 11 to 34 months. For the four remaining cylinders, one was analyzed six times over a 13 month period, two were analyzed seven times over 13 and 14 months, and one was analyzed nine times over a period of 21 months.

For the 16 regression equations; five slopes (m) were 0.000 ppm change/month, four were negative and seven were positive with an average value of $\bar{m}$ = +0.001 ppm change/month and a standard deviation of the slope of s_m = 0.010 ppm change/month. Based on the Student's t-test, the probability of average slopes of 0.001 or greater due to chance causes alone is greater than 50 percent. Thus, there was no reason to reject the hypothesis that the true mean slope was zero.

TABLE 5. STABILITY DATA FOR CO/NITROGEN IN ALUMINUM CYLINDERS

ANALYSIS NO.	INITIAL ANALYSIS			SUBSEQUENT ANALYSIS[a]																			
Cylinder No.	Date	Conc. (ppm)	Source[b]	T	ppm	T	ppm	T	ppm	T	ppm	T	ppm	T	ppm	T	ppm	T	ppm		m	b	s_y
JJ1702-38	03-01-82	5.6	A	12	5.6																		
JJ1394-39	03-01-82	5.6	A	12	5.6																0.000	5.60	0.000
JJ1970-40	03-01-82	5.6	A	13	5.4																0.000	5.60	0.000
JJ9708-41	03-01-82	5.6	A	13	5.4																-0.015	5.60	0.141
JJ1427-42	10-01-79	7.1	A	33	7.1																-0.015	5.60	0.141
SGAL589-48	08-01-81	7.8	B	11	8.0																0.000	7.10	0.000
JJ1434-43	04-01-80	8.2	A	34	8.3																+0.018	7.80	0.141
JJ1361-44	04-01-80	8.2	A	31	8.1																+0.003	8.20	0.071
SGCC27219-35	09-30-81	9.3	C	3	9.3	5	9.5	8	9.6	11	9.5	13	9.5								-0.003	8.20	0.071
SGCC27238-33	09-10-81	9.6	C	3	9.6	5	9.5	8	9.5	11	9.4	14	9.5	15	9.4						+0.018	9.33	0.122
SGCC27229-37	09-23-81	8.4	C	2	8.3	6	8.5	8	7.7	9	8.4	12	8.5	14	8.3	19	8.5	21	8.5		-0.012	9.60	0.082
SGCC27235-36	09-01-81	9.4	C	3	9.4	5	9.1	8	9.4	11	9.4	14	9.5	18	9.6						+0.009	8.25	0.255
JJ9520-45	09-01-80	10.5	A	29	10.6																+0.014	9.28	0.153
JJ1256-46	09-01-80	10.5	A	29	10.6																+0.003	10.50	0.071
JJ1889-47	10-01-81	13.6	A	16	13.6																+0.003	10.50	0.071
JJ1661-60	08-01-80	15.2	A	23	15.2																0.000	13.60	0.000
																					0.000	15.20	0.000
Summary Statistics: $\bar{m}$ = +0.001 ppm change/month; s_m = 0.010 ppm change/month; s_{yp} = 0.15 ppm																							
JJ9621-62	03-01-82	19.1	A	11	19.2																+0.009	19.10	0.071
JJ1632-61	03-01-82	19.2	A	11	19.2																0.000	19.20	0.000
JJ1623-63	02-01-81	20.1	A	17	20.2																+0.006	20.10	0.071
SGAL677-76	08-01-81	20.1	B	11	20.4																+0.027	20.10	0.212
JJ1646-66	09-01-80	21.1	A	26	21.3																+0.008	21.10	0.141
CAL1812-77	03-01-80	24.6	B	17	24.3																-0.018	24.60	0.212
JJ9558-64	03-01-81	25.1	A	11	25.2																+0.009	25.10	0.071
JJ1126-67	03-01-81	25.1	A	16	25.3																+0.013	25.10	0.141
JJ1625-65	03-01-81	25.2	A	11	25.2																0.000	25.20	0.000
JJ1547-68	09-01-80	39.7	A	26	39.4																-0.012	39.70	0.212
SGAL629-75	08-01-81	42.2	B	11	42.6																+0.036	42.20	0.283
JJ1420-69	03-01-81	43.9	A	19	44.1																+0.011	43.90	0.141
JJ1174-70	03-01-81	43.9	A	16	44.2																+0.019	43.90	0.212
JJ9511-71	03-01-81	43.9	A	16	44.2																+0.019	43.90	0.212
AAL1303-73	06-16-80	45.4	B	21	45.3	31	45.4														-0.001	45.38	0.06
FF6134	02-01-81	46.4	B	7	46.5	14	45.8														-0.043	46.53	0.38
AAL570-74	01-16-80	45.4	B	18	45.7	31	45.8														+0.015	45.42	0.21
Summary Statistics: $\bar{m}$ = +0.006 ppm change/month; s_m = 0.010 ppm change/month; s_{yp} = 0.20 ppm																							
BAL2183-78	09-01-81	104.0	A	17	104.0																0.000	104.0	0.00
BAL2206-79	09-01-81	104.0	A	17	104.0																0.000	104.0	0.00
BAL2358-80	09-01-81	104.0	A	17	104.0																0.000	104.0	0.00
CC6055-85	06-18-81	252.9	B	6	253.0	9	253.0														+0.012	252.9	0.06
BAL2198-81	09-01-81	504.0	A	17	504.0																0.000	504.0	0.00
BAL2185-82	09-01-81	504.0	A	17	504.0																0.000	504.0	0.00
BAL2194-83	09-01-81	504.0	A	17	504.0																0.000	504.0	0.00

[a] T = Time in months since the initial analysis

[b] See Table 3

TABLE 5. STABILITY DATA FOR CO/NITROGEN IN ALUMINUM CYLINDERS
(cont'd)

ANALYSIS NO.	INITIAL ANALYSIS			SUBSEQUENT ANALYSIS[a]																			
Cylinder No.	Date	Conc. (ppm)	Source[b]	T	ppm	T	ppm	T	ppm	T	ppm	T	ppm	T	ppm	T	ppm		a	b	s_y
BAL2425-84	09-01-81	504.0	A	17	504.0														0.000	504.0	0.00
FF9320-99	06-19-81	935.6	B	7	930.2	21	932.5												-0.103	933.7	2.71
FF1828-100	04-01-78	1008.0	B	15	1006.0	23	995.0	38	1008.0										-0.058	1005.4	6.24
LL10999-97	06-18-81	1010.8	B	9	1010.6	23	1007.0												-0.173	1011.3	2.14
LL9916-98	06-18-81	1010.8	B	7	1012.4	11	1007.0												-0.281	1011.8	2.77
CC17145-96	12-09-81	1027.0	B	14	1013.0														-1.000	1027.0	9.90
FF1995-105	04-01-78	1041.0	B	15	1039.0	23	1032.0	25	1047.0										-0.021	1040.1	6.19
FF2011-107	04-01-78	1048.0	B	15	1040.0	19	1040.0	27	1039.0										-0.348	1047.0	4.19
FF3049-104	03-01-79	1056.0	B	8	1056.0	16	1059.0												+0.188	1055.5	1.73
Summary Statistics: $\bar{m}$ = -0.112 ppm change/month; s_m = 0.268 ppm change/month; s_{yp} = 3.98 ppm																							
FF2388-103	10-01-78	2595.0	B	9	2591.0	8	2571.0												-1.333	2597.7	12.86
FF2988-106	01-01-79	2603.0	B	7	2607.0	8	2618.0	16	2588.0										-0.955	2611.4	12.41
FF2998-120	02-01-79	2647.0	B	6	2665.0	14	2592.0	28	2628.0	37	2673.0								+0.413	2632.0	30.85
FF6082-118	11-01-80	4470.0	B	13	4555.0	22	4590.0												+5.531	4473.8	61.71
CC9453-92	02-18-81	4900.0	B	12	4799.0														-8.417	4900.0	71.42
FF3032-110	02-01-80	4921.0	B	11	4970.0														+4.455	4921.0	34.65
FF1881-108	07-01-79	4934.0	B	8	4940.0	11	4995.0												+4.557	4927.5	33.62
FF6078-17	07-01-79	4948.0	B	6	4948.0	11	4857.0	20	4867.0	30	4935.0								-0.951	4923.7	45.18
FF3530-111	02-01-80	4964.0	B	4	5000.0	7	5034.0	12	5078.0										+9.603	4963.8	48.62
FF2415-114	02-01-80	4988.0	B	6	5004.0	9	4958.0	14	4975.0	22	5029.0								+1.457	4975.9	27.23
LL1522-90	03-02-81	4992.0	A	23	5048.0														+2.435	4992.0	39.60
FF2895-116	02-01-80	5003.0	B	7	4996.0	11	4968.0	19	5030.0	31	5082.0								+2.922	4976.1	43.08
CAL4746-102	03-01-82	5011.0	B	5	5016.0	15	4918.0												-6.714	5026.4	55.19
FF8007-121	06-01-81	5030.0	B	8	5041.0	14	5066.0												+2.507	5027.3	18.45
FF5908-109	09-01-80	5052.0	B	7	5053.0	15	5023.0												-1.976	5057.2	17.04
FF3112-101	02-01-81	5096.0	B	5	5052.0	10	5046.0	12	5058.0	19	5077.0								-0.715	5072.4	20.50
CC4239-91	07-07-81	5102.0	B	12	5157.0														+4.583	5102.0	38.89
FF2393-122	05-01-79	5135.0	B	9	5162.0	21	5228.0	31	5181.0										+1.973	5146.4	39.18
FF4427-89	12-11-81	5136.0	A	7	4977.0	13	5076.0												-5.114	5097.1	80.29
FF2987-113	05-01-79	5140.0	B	13	5153.0	18	5060.0	21	5268.0	30	5222.0								+3.131	5117.2	79.98
FF6056-115	04-01-81	5188.0	B	11	5301.0	16	5307.0												+7.903	5194.2	67.04
FF424-119	03-01-79	5201.0	B	5	5201.0	12	5240.0	15	5174.0	20	5175.0								-1.353	5212.9	26.98
FF6668-87	09-16-81	5210.0	A	5	4921.0	11	5163.0												-2.802	5112.9	155.08
FF8597-88	12-11-81	5231.0	A	6	5058.0	13	5173.0												-3.886	5178.6	88.05
FF8902-86	09-16-81	5252.0	A	5	4971.0	10	4974.0	18	5073.0										-7.460	5129.0	131.81
FF763-112	09-01-78	5383.0	B	10	5323.0	11	5251.0												-9.568	5316.0	66.09
Summary Statistics: $\bar{m}$ = +0.009 ppm change/month; s_m = 4.92 ppm change/month; s_{yp} = 59 ppm																							

[a] T = Time in months since the initial analysis

[b] See Table 3

The precision of analysis as estimated by the pooled standard deviation of the measured concentrations was s_{yp} = 0.15 ppm. The approximate 95 percent probability interval (excluding bias) for the uncertainty of a pollutant concentration estimated by one analysis was $\pm$ 2 s_{yp} = 2(0.15) = 0.3 ppm. For a measured concentration value of 10 ppm, the uncertainty was $\pm$ 0.3 ppm (or $\pm$ 3 percent). Likewise for a measured concentration of 5 ppm, the relative uncertainty was $\pm$ 6 percent.

Based on the average slope it was concluded that CO/N_2 in aluminum cylinders at concentrations from 5 to 15 ppm is stable over time periods greater than 18 months. Also, from a practical point of view, the above precision estimate indicates that the uncertainty associated a single analysis ($\pm$ 3 percent) at concentrations near 10 ppm is acceptable while the uncertainty of a single analysis ($\pm$ 6 percent) at concentrations near 5 ppm may not be acceptable, in which case a second analysis should be made.

Concentration Range 19 to 46 ppm--

For CO/nitrogen in aluminum cylinders, 19 to 46 ppm, there were 17 cylinders with concentrations ranging from 19.1 to 46.5 ppm (see Table 5). Fourteen of the cylinders were analyzed twice over time periods ranging from 11 to 26 months. The three remaining cylinders were analyzed three times, over time periods ranging from 14 to 31 months.

The 17 calculated regression equation slopes include four negative, eleven positive, and two zero values. The average slope was $\bar{m}$ = +0.006 ppm change/month and the standard deviation of the slopes about the average was s_m = 0.018 ppm change/month (see summary statistics in Table 5). Using the Student's t-test to test the hypothesis that the true slope was zero yielded:

$$t = \frac{\bar{m} - 0}{s_m/\sqrt{k}} = \frac{+0.006-0}{0.018/\sqrt{17}} = 1.374$$

Comparing the calculated t value to tabulated values for 16 degrees of freedom indicate that average slopes of 0.006 ppm change/month or larger can be expected to occur more than 15 percent of the time due to

chance causes alone. Thus, there was no reason to reject the hypothesis that the true mean slope was zero. An approximate 95 percent probability interval for slopes in this category was $\bar{m} \pm 2\ s_m$ = +0.006 $\pm$ 0.018 ppm change/month. For an 18 month period, for example, the 95 percent probability interval for total change in concentration based on the distribution of the slopes was +0.108 $\pm$ 0.324 ppm (-0.216 to +0.432 ppm) and for a median concentration value of 30 ppm the interval expressed as a percent was -0.7 percent to +1.4 percent.

The precision of analysis as estimated by the pooled standard deviation of the measured concentrations was s_{yp} = 0.20 ppm (see Table 5). The approximate 95 percent probability interval for the uncertainty (excluding bias) of a CO/nitrogen concentration estimated by one analysis was $\pm$ 2 s_{yp} = 0.40 ppm or $\pm$1.3 percent at a concentration of 30 ppm.

Based on the above results it was concluded that CO/N_2 in aluminum cylinders at concentrations of 19 to 46 ppm is stable for periods greater than 18 months and the precision of analysis is such that repeated Protocol No. 2 analyses over that time period are not necessary.

Concentration Range 100 to 1000 ppm--

For CO/nitrogen in aluminum cylinders, 100 to 1000 ppm, there were 16 cylinders with measured concentrations ranging from 104 to 1056 ppm (see Table 5). Three of the cylinders were analyzed four times over time periods ranging from 25 to 38 months, eight of the cylinders were analyzed three times over time periods ranging from 9 to 23 months and the rest of the cylinders were analyzed twice over time periods ranging from 14 to 17 months.

The 16 calculated regression equation slopes include seven negative, two positive and seven zero values. The average slope was $\bar{m}$ = -0.112 ppm change/month and the standard deviation of the slopes about the average was s_m = 0.268 ppm change/month (see summary statistics in Table 5). Using the Student's t-test to test the hypothesis that the true mean slope was zero yielded:

$$t = \frac{\bar{m} - 0}{s_m/\sqrt{k}} = \frac{-0.004}{0.013/\sqrt{10}} = 0.973$$

Comparing the calculated t value to tabulated values for 15 degres of freedom indicate that average slopes of 0.112 ppm change/month or larger can be expected to occur more than 15 percent of the time due to chance causes alone. Thus, there was no reason to reject the hypothesis that the true mean slope was zero. An approximate 95 percent probability interval for slopes in this category was $\bar{m} \pm 2\ s_m$ = $-0.112 \pm .536$ ppm change/month. For an 18 month period, for example, the 95 percent probability interval for total change in concentration based on the distribution of slopes was -2.016 ± 9.648 ppm (-11.664 to +7.632 ppm) and for a median concentration value of 500 ppm the interval expressed as a percent was -2.3 percent to 1.5 percent.

The precision of analysis as estimated by the pooled standard deviation of the measured concentrations was s_{yp} = 3.98 ppm (see Table 5). The approximate 95 percent probability interval for the uncertainty (excluding bias) of a CO/nitrogen concentration estimated by one analysis was $\pm 2\ s_{yp}$ = 7.96 ppm or $\pm$1.6 percent at a concentration of 500 ppm.

Based on the above results it was concluded that CO/N_2 in aluminum cylinders at concentrations between 100 and 1000 ppm was stable for time periods greater than 18 months and that the precision of analysis indicates that repeated Protocol No. 2 analyses over that time period are not necessary.

Concentration Range 2500 to 5000 ppm--

For CO/nitrogen in aluminum cylinders, 2500 to 5000 ppm, there were 26 cylinders with measured concentrations ranging from 2591 to 5323 ppm (see Table 5). Seven cylinders were analyzed five times over time periods ranging from 19 to 31 months, four of the cylinders were analyzed four times over time periods ranging from 12 to 31 months, eleven of the cylinders were analyzed three times over time periods ranging from 11 to 22 months, and the remaining four cylinders were analyzed twice over time periods ranging from 11 to 23 months.

The 26 calculated regression equation slopes included thirteen negative and thirteen positive values. The average slope was $\bar{m}$ = +0.009 ppm change/month and the standard deviation of the slopes

about the average was s_m = 4.92 ppm change/month (see summary statistics in Table 5). Using the Student's t-test to test the hypothesis that the true mean slope was zero yielded:

$$t = \frac{\bar{m} - 0}{s_m/\sqrt{k}} = \frac{+0.009 - 0}{4.92/\sqrt{26}} = 0.009$$

Comparing the calculated t value to tabulated values for 25 degrees of freedom indicate that average slopes of 0.009 ppm change/month or larger can be expected to occur more than 80 percent of the time due to chance causes alone. Thus, there was no reason to reject the hypothesis that the true mean slope was zero. An approximate 95 percent probability interval for slopes in this category was $\bar{m} \pm 2\ s_m$ = +0.009 $\pm$ 9.844 ppm change/month. For an 18 month period, for example, the 95 percent probability interval for total change in concentration based on the distribution of the slopes was +0.162 $\pm$ 177.192 ppm (-177.030 to +177.354 ppm) and for a median concentration value of 3750 ppm the interval expressed as a percent was -4.7 percent to +4.7 percent.

The precision of analysis as estimated by the pooled standard deviation of the measured concentrations was s_{yp} = 59 ppm (see Table 5). The approximate 95 percent probability interval for the uncertainty (excluding bias) of a CO/nitrogen concentration estimated by one analysis was $\pm$ 2 s_{yp} = 118 ppm or $\pm$ 3 percent at a concentration of 3750 ppm.

Based on the above results it was concluded that CO/nitrogen in aluminum cylinders at concentrations between 2500 and 5000 ppm is stable over time periods greater than 18 months and that the precision of analysis indicates that repeated Protocol No. 2 analyses over that time interval are not necessary.

Nitric Oxide In Nitrogen Contained in Aluminum Cylinders

Stability data from 103 aluminum cylinders containing nitric oxide with a balance gas of nitrogen were analyzed. The stability data,

cylinder number, date of initial analysis, initial concentration, method of initial analysis, months (T) since the initial analysis and the analyzed concentration in ppm are contained in Table 6. Also contained in this table are the linear regression constants, slope (m) and intercept (b), calculated from analyzed concentrations versus months since the initial analysis and the standard deviation (s_y) of the y-axis values (nitric oxide concentrations). The data were subdivided into concentation ranges and analyzed according to a median concentration. The concentration ranges were selected according to what appeared to be natural gaps in the concentration distribution of the data. Also, the use of relatively small concentration intervals allows one to assume equal variances for the analysis. These data were divided into three concentration ranges 10 to 22, 43 to 55, and 80 to 113 ppm.

Concentration Range 10 to 22 ppm--

For NO/nitrogen in aluminum cylinders, 10 to 22 ppm, there were 7 cylinders with measured concentrations ranging from 10.6 to 22.3 ppm (see Table 6). All of the cylinders were analyzed three times over time periods ranging from 16 to 25 months.

The seven calculated regression equation slopes included four negative and three positive values. The average slope was $\bar{m}$ = -0.003 ppm change/month and the standard deviation of the slopes about that average was s_m = 0.014 ppm change/month (see summary statistics in Table 6). Using the Student's t-test to test the hypothesis that the true mean slope was zero yielded:

$$t = \frac{\bar{m} - 0}{s_m/\sqrt{k}} = \frac{+0.009-0}{4.922/\sqrt{26}} = 0.009$$

Comparing the calculated t value to tabulated values for 6 degrees of freedom indicate that average slopes of 0.003 ppm change/month or larger can be expected to occur more than 50 percent of the time due to chance causes alone. Thus, there was no reason to reject the hypothesis that the true mean slope was zero. An approximate 95 percent probability interval for slopes in this category was $\bar{m} \pm 2\ s_m$ = -0.003 $\pm$ 0.028 ppm change/month. For an 18 month period, for example,

TABLE 6. STABILITY DATA FOR NO/NITROGEN IN ALUMINUM CYLINDERS

ANALYSIS NO.	INITIAL ANALYSIS			SUBSEQUENT ANALYSIS[a]													
Cylinder No.	Date	Conc. (ppm)	Source[b]	T	ppm	T	ppm	T	ppm	T	ppm	T	ppm	T	ppm	m	b	s_y
AAL6466-131	06-11-81	10.7	B	6	10.6	17	10.8									+0.007	10.63	0.10
CAL6975-128	06-01-81	11.7	A	15	11.7	22	11.6									-0.004	11.71	0.06
BAL1701-127	12-01-81	19.7	A	9	20.0	16	19.8									+0.008	19.77	0.15
BAL2131-126	09-01-81	19.6	A	10	19.4	19	19.3									-0.016	19.59	0.15
LL4313-130	07-01-79	19.8	A	11	20.2	25	20.2									+0.015	19.88	0.23
BAL1752-129	02-01-81	19.9	A	19	19.9	23	19.8									-0.003	19.91	0.06
LL4326-125	12-01-81	21.6	A	8	22.3	16	21.2									-0.025	21.90	0.56
Summary Statistics: $\bar{m}$ = -0.003 ppm change/month; s_m = 0.014 ppm change/month; s_{yp} = 0.25																		
FF4638-181	04-01-78	43.6	B	42	43.6	58	44.0									+0.005	43.55	0.23
FF4789-172	12-01-78	43.7	D	4	43.6	12	43.6									-0.007	43.67	0.06
FF4856-166	02-01-79	47.7	B	6	47.6	13	47.6	17	46.3	24	46.4					-0.063	47.88	0.71
CC14342-163	12-19-80	48.1	B	5	48.3	16	48.5									+0.024	48.13	0.20
CAL1929-146	04-01-81	48.1	B	12	48.1											0.000	48.10	0.00
SGAL2926-175	01-01-81	48.0	D	7	47.8	17	47.1									-0.054	48.07	0.47
SGAL2907-171	02-01-81	48.5	D	9	48.5	16	48.4									-0.006	48.52	0.06
LL9703-148	04-01-81	49.3	A	7	49.7	16	50.1									+0.050	49.32	0.40
LL9924-162	02-09-82	49.8	B	13	49.8											0.000	49.80	0.00
LL9622-158	04-01-81	49.9	A	10	49.5	11	51.8									+0.086	49.80	1.23
CAL6996-144	09-01-81	50.1	A	8	49.6	19	50.1									+0.003	49.91	0.29
LL376-150	12-01-80	50.1	A	7	50.1	14	51.5									+0.100	49.87	0.81
LL1027-156	12-01-80	50.1	A	7	50.1	14	49.5									-0.043	50.20	0.35
SGAL557-174	12-01-80	50.3	D	7	50.7	18	51.2									+0.050	50.32	0.45
LL330-153	12-01-80	50.5	A	7	50.2	14	49.4									-0.079	50.58	0.57
LL1809-151	12-01-80	50.6	A	7	49.5	14	49.0									-0.114	50.50	0.82
LL1638-155	12-01-80	50.7	A	7	49.9	14	48.8									-0.136	50.75	0.95
LL10456-157	12-01-80	51.0	A	7	50.2	14	49.3									-0.121	51.02	0.85
LL4375-149	11-01-81	51.6	A	9	52.1	14	52.4									+0.057	51.60	0.40
CAL7214-145	05-01-81	52.2	A	12	52.2	18	52.0									-0.010	52.23	0.12
LL4388-154	01-01-81	52.3	A	7	52.3	14	51.3									-0.071	52.47	0.58

[a] T = Time in months since the initial analysis

[b] See Table 3

TABLE 6. STABILITY DATA FOR NO/NITROGEN IN ALUMINUM CYLINDERS
(cont'd)

ANALYSIS NO.	INITIAL ANALYSIS			SUBSEQUENT ANALYSIS[a]																			
Cylinder No.	Date	Conc. (ppm)	Source[b]	T	ppm	T	ppm	T	ppm	T	ppm	T	ppm	T	ppm	T	ppm	m	b	s_y
CAL1548-179	03-01-82	52.3	C	7	53.9	13	52.1											-0.009	52.82	0.99
LL9630-152	12-01-80	52.5	A	7	52.0	14	50.9											-0.114	52.60	0.82
LL4312-159	01-01-81	53.1	A	6	52.3	13	50.9											-0.170	53.18	1.11
FF6954-136	08-01-80	55.0	E	18	55.0	29	54.6											-0.012	55.06	0.23
Summary Statistics: $\bar{m}$ = -0.025 ppm change/month; s_m = 0.070 ppm change/month; s_{yp} = 0.64																							
FF4931-132	03-01-80	80.3	E	12	80.9	21	81.1	31	80.4									+0.006	80.58	0.39
FF13659-138	09-01-79	80.4	E	13	80.4	21	83.0	27	82.6	35	81.7							+0.059	80.49	1.21
CAL2435-139	06-01-81	83.8	E	2	83.9	14	82.8											-0.078	83.92	0.61
CAL530-137	06-01-81	84.1	E	2	84.1	14	83.7	24	84.2									-0.001	84.03	0.22
CAL911-133	06-01-81	83.8	E	6	84.2	17	84.0											+0.008	83.94	0.20
SP10300-178	12-01-81	88.0	C	10	87.9	17	87.9											-0.006	87.99	0.06
FF1726-168	05-01-79	92.7	B	6	91.7	14	92.7	21	93.3									+0.042	92.17	0.66
JJ1027-160	07-01-81	93.2	A	7	95.9	18	94.2											+0.037	94.13	1.37
JJ1036-161	01-01-80	93.6	A	19	93.7	36	94.9											+0.036	93.42	0.72
FF6817-142	12-09-81	93.7	B	5	95.7	13	95.1											+0.091	94.29	1.03
FF4866-170	03-01-78	94.2	B	12	94.2													0.000	94.20	0.00
FF3101-165	02-01-80	94.1	B	3	94.9	9	94.5	13	95.3	16	95.2							+0.059	94.32	0.50
FF2907-169	02-01-80	95.7	D	4	95.7	6	96.2	9	94.9	12	97.0							+0.061	95.52	0.77
SP10800-176	04-01-80	95.9	C	10	96.4	16	96.4	23	102.6	29	102.6							+0.269	94.59	3.49
SP10777-177	10-01-80	96.5	C	6	102.7	14	98.8	25	96.5									-0.075	94.47	2.93
FF9456-167	11-01-80	96.4	B	6	93.8	13	93.8											-0.099	96.69	1.90
FF8423-180	08-01-79	97.4	C	11	97.5	21	97.8											+0.019	97.37	0.21
CC6008-184	01-01-81	97.6	A	6	99.3	13	100.0											+0.182	97.81	1.23
FF4056-134	05-01-80	98.1	E	11	98.1	21	98.4	35	98.0									-0.001	98.16	0.17
FF6725-143	08-31-81	98.1	B	6	102.1	12	101.3	19	99.1									+0.028	99.89	1.86
FF17392-164	02-01-82	98.2	B	10	96.9	17	96.9											-0.140	98.13	0.75
FF6737-141	11-01-79	98.7	E	38	98.4	43	98.7											-0.003	98.68	0.17
LL3510-187	08-01-79	98.7	A	23	99.3	30	100.0											+0.039	98.64	0.65
CC5473-189	08-01-81	98.7	E	12	100.0													+0.108	98.70	0.92

[a] T = Time in months since the initial analysis

[b] See Table 3

TABLE 6. STABILITY DATA FOR NO/NITROGEN IN ALUMINUM CYLINDERS
(cont'd)

| ANALYSIS NO. | INITIAL ANALYSIS | | | SUBSEQUENT ANALYSIS[a] | | |

TABLE 6. STABILITY DATA FOR NO/NITROGEN IN ALUMINUM CYLINDERS
(cont'd)

ANALYSIS NO.	INITIAL ANALYSIS			SUBSEQUENT ANALYSIS[a]																			
Cylinder No.	Date	Conc. (ppm)	Source[b]	T	ppm	T	ppm	T	ppm	T	ppm	T	ppm	T	ppm	T	ppm	m	b	s_y
FF14321-192	06-01-81	102.1	B	5	100.2	13	102.1											+0.022	101.33	1.10
CC14335-231	12-23-80	102.1	C	10	103.3	12	103.4											+0.112	102.11	0.72
FF6517-232	02-01-81	103.0	D	3	103.0	6	103.0	9	102.0	12	102.0	14	102.0	18	102.0	21	102.0	-0.060	103.00	0.52
CC5635-233	02-01-81	103.0	E	13	103.0	25	103.0											0.000	103.00	0.00
FF8753-199	06-01-79	103.4	B	7	103.9	9	104.5	12	103.9	15	104.6							+0.070	103.46	0.49
LL3098-197	01-01-80	104.0	B	18	102.1													-0.106	104.00	1.34
LL1938-195	08-01-80	104.4	B	1	103.4	4	102.9	16	102.8									-0.068	103.73	0.73
CC6976-210	08-15-81	104.6	B	9	103.9	20	104.4											-0.008	104.37	0.36
CC27087-211	09-16-81	106.3	B	6	106.6	15	107.8	20	107.0									+0.053	106.39	0.65
CC34063-212	09-16-81	106.3	B	6	106.6	15	109.2	17	106.5									+0.087	106.33	1.37
FF1982-190	05-01-79	107.1	B	6	105.5	13	107.4	21	107.9	29	105.1							-0.023	106.92	1.23
FF2935-200	03-01-79	107.8	B	5	107.5	13	102.4											-0.436	108.52	3.04
FF2791-227	02-01-80	109.1	B	12	110.6													+0.125	109.10	1.06
FF2796-198	02-01-80	110.4	B	12	110.4	16	110.4											0.000	110.40	0.00
FF16881-229	09-14-81	111.8	B	13	114.36													+0.197	111.80	1.81
LL4331-213	01-01-81	112.0	A	6	112.0	14	108.0											-0.297	112.65	2.31
FF2917-194	07-01-80	112.3	B	7	111.1	12	110.4											-0.159	112.28	0.96
LL4349-217	06-01-81	113.0	A	9	112.0	16	114.0	21	110.9									-0.052	113.07	1.33

Summary Statistics: $\bar{m}$ = -0.009 ppm change/month; s_m = 0.112 ppm change/month; s_{yp} = 1.19

[a] T = Time in months since the initial analysis

[b] See Table 3

the 95 percent probability interval for total change in concentration based on the distribution of the slopes was -0.054 $\pm$ 0.504 ppm (-0.558 to 0.450 ppm) and for a median concentration value of 16 ppm the interval expressed as a percent was -3.5 percent to +2.8 percent.

The precision of analysis as estimated by the pooled standard deviation of the measured concentrations was s_{yp} = 0.25 ppm (see Table 6). The approximate 95 percent probability interval for the uncertainty (excluding bias) of a NO/nitrogen concentration estimated by one analysis was $\pm 2\ s_{yp}$ = 0.50 ppm or $\pm$3.1 percent at a median concentration of 16 ppm.

Based on the above results it was concluded that NO/nitrogen in aluminum cylinders at concentrations between 10 and 22 ppm is stable over time periods as long as 18 months and that the precision of analysis indicates that repeated Protocol No. 2 analyses over that time interval are not necessary.

Concentration Range 43 to 55 ppm--

For NO/nitrogen in aluminum cylinders, 43 to 55 ppm, there were 25 cylinders with measured concentrations ranging from 43.6 to 55 ppm (see Table 6). One of the cylinders was analyzed five times over a 24 month time period, twenty-two cylinders were analyzed three times over time periods ranging from 11 to 58 months, and the remaining two cylinders were analyzed twice over time periods of 12 and 13 months.

The 25 calculated regression slopes include fifteen negative, eight positive and two zero values. The average slope was $\bar{m}$ = -0.025 ppm change/month and the standard deviation of the slopes about the average was s_m = 0.070 ppm change/month (see summary statistics in Table 6). Using the Student's t-test to test the hypothesis that the true mean slope was zero yielded:

$$t = \frac{\bar{m} - 0}{s_m/\sqrt{k}} = \frac{-0.025 - 0}{0.070/\sqrt{25}} = 1.79$$

Comparing the calculated t value to tabulated values for 24 degrees of freedom indicate that average slopes of 0.025 ppm change/month or

larger can be expected to occur approximately 10 percent of the time due to chance causes alone. Thus, there was no reason to reject the hypothesis that the true mean slope was zero. An approximate 95 percent probability interval for slopes in this category was $\bar{m} \pm 2$ s_m = -0.025 $\pm$ 0.140 ppm change/month. For an 18 month period, for example, the 95 percent probability interval for total change in concentration based on the distribution of the slopes was -0.450 $\pm$ 2.52 ppm (-2.97 to +2.07 ppm) and for a median concentration value of 49 ppm the interval expressed as a percent was -6.1 percent to +4.2 percent.

The precision of analysis as estimated by the pooled standard deviation of the measured concentration was s_{yp} = 0.64 ppm (see Table 6). The approximate 95 percent probability interval for the uncertainty (excluding bias) of a NO/nitrogen concentration estimated by one analysis was ± 2 s_{yp} = 1.28 or $\pm$2.6 percent at a concentration of 49 ppm.

Based on the above results it was concluded that NO/nitrogen in aluminum cylinders at concentrations between 43 and 55 ppm is stable over time periods greater than 18 months and that the precision of analysis indicates that repeated Protocol No. 2 analyses over that time interval are not necessary.

Concentration Range 80 to 113 ppm--

For NO/nitrogen in aluminum cylinders, 80 to 113 ppm, there were 71 cylinders with measured concentrations ranging from 80.3 to 114 ppm (see Table 6). One of the cylinders was analyzed eight times over 21 months, nine of the cylinders were analyzed five times over time periods ranging from 12 to 35 months, twelve of the cylinders were analyzed three times over time periods ranging from 13 to 36 months and the remaining 10 cylinders were analyzed twice over time periods ranging from 10 to 18 months.

The 71 calculated regression equation slopes include thirty-six negative, thirty-one positive and four zero values. The average slope was $\bar{m}$ = -0.009 ppm change/month and the standard deviation of the slopes about that average was s_m = 0.112 ppm change/month (see summary statistics in Table 6). Using the Student's t-test to test the hypothesis that the true mean slope was zero yielded:

$$t = \frac{\bar{m} - 0}{s_m/\sqrt{k}} = \frac{-0.009-0}{0.112/\sqrt{71}} = 0.677$$

Comparing the calculated t value to tabulated values for 70 degrees of freedom indicate that average slopes of 0.009 ppm change/month or larger can be expected to occur more than 50 percent of the time due to chance causes alone. Thus, there was no reason to reject the hypothesis that the true mean slope was zero. An approximate 95 percent probability intervals for slopes in this category was $\bar{m} \pm 2\ s_m$ = -0.009 ± 0.225 ppm change/month. For an 18 month period, for example, the 95 percent probability interval for total change in concentration based on the distribution of the slopes was -0.162 ± 4.032 ppm (-4.194 to 3.870 ppm) and for a median concentration value of 97 ppm the interval expressed as a percent was -4.3 percent to 4.0 percent.

The precision of analysis as estimated by the pooled standard deviation of the measured concentrations was s_{yp} = 0.72 ppm (see Table 6). The approximate 95 percent probability interval for the uncertainty (excluding bias) of a NO/nitrogen concentration estimated by one analysis was $\pm 2\ s_{yp}$ = 1.44 ppm or $\pm$ 1.5 percent at a concentration of 97 ppm.

Based on the above results it was concluded that NO/nitrogen in aluminum cylinders at concentrations between 80 to 113 ppm is stable for time periods greater than 18 months and that the precision of analysis indicates that repeated Protocol No. 2 analyses over that time period are not necessary.

Sulfur Dioxide In Nitrogen Contained In Aluminum Cylinders

Stability data for seventy-five aluminum cylinders containing sulfur dioxide with a balance gas of nitrogen were analyzed. This stability data, cylinder number, date of initial analysis, initial concentration, method of initial analysis, months since the initial analysis (T) and the analyzed concentration in ppm are contained in Table 7. Also contained in this table are the linear regression coefficients, slope (m) and intercept (b), calculated from the analyzed concentrations

TABLE 7. STABILITY DATA FOR SO_2/NITROGEN IN ALUMINUM CYLINDERS

ANALYSIS NO.	INITIAL ANALYSIS			SUBSEQUENT ANALYSIS[a]													
Cylinder No.	Date	Conc. (ppm)	Source[b]	T	ppm	T	ppm	T	ppm	T	ppm	T	ppm	T	ppm	m	b	s_y
LL3669-235	10-01-81	9.3	A	8	9.6	15	9.8									+0.033	9.31	0.25
CAL7512-236	02-01-82	9.4	A	7	9.1	13	8.9									-0.039	9.39	0.25
BAL1932-238	07-01-81	9.5	A	11	9.6	17	9.5									+0.001	9.52	0.06
BAL1979-237	07-01-81	9.6	A	7	9.8	16	9.8									+0.012	9.64	0.12
BAL456-239	07-01-81	9.8	A	12	9.8	17	9.9									+0.005	9.79	0.06
BAL836-234	02-01-82	10.1	A	6	10.0	14	10.0									-0.007	10.08	0.06
LL4500-240	12-01-81	10.2	A	8	10.5	15	10.2									+0.001	10.29	0.17
LL4327-241	01-01-82	10.2	A	7	10.1	15	9.8									-0.027	10.23	0.21
LL11009-243	02-01-81	10.5	A	11	10.5											0.000	10.50	0.00
LL3737-244	01-23-81	21.5	B	6	21.4	18	21.3									-0.011	21.49	0.10
Summary Statistics: $\bar{m}$ = -0.003 ppm change/month; s_m = 0.020 ppm change/month; s_{yp} = 0.15																		
LL11521-262	11-01-81	49.2	A	12	49.8											+0.050	49.20	0.42
CAL7286-246	01-01-82	49.3	E	18	50.3											+0.056	49.30	0.71
BAL2486-267	10-01-81	49.4	A	12	51.4											+0.167	49.40	1.41
BAL2378-268	10-01-81	50.4	A	15	50.0											-0.027	50.40	0.28
LL4335-273	08-31-81	50.5	B	3	50.6	35	50.3									-0.007	50.56	0.15
BAL2494-261	10-01-81	50.6	A	14	50.0											-0.043	50.60	0.42
BAL2421-259	10-01-81	51.0	A	11	51.4											+0.036	51.00	0.28
LL10491-266	10-01-80	51.0	A	26	51.1											+0.004	51.00	0.07
AAL6808-283	04-01-82	51.1	C	12	51.6											+0.042	51.10	0.35
BAL2402-269	10-01-81	51.4	A	12	51.9											+0.042	51.40	0.35
CC4452-274	11-13-81	51.5	B	8	50.8	16	50.5									-0.063	51.43	0.51
AAL5293-284	04-01-82	51.6	C	12	51.5											-0.008	51.60	0.07
BAL2398-260	10-01-81	51.7	A	11	51.7											0.000	51.70	0.00
CAL7691-247	01-01-82	52.5	D	12	52.1											-0.033	52.50	0.28
BAL1704-265	03-01-81	53.3	A	17	52.8											-0.029	53.30	0.35
CAL7726-250	01-01-82	55.1	E	3	55.3	11	55.4									+0.024	55.15	0.15
CAL7718-253	06-01-82	56.4	D	11	54.3											-0.191	56.40	1.49
Summary Statistics: $\bar{m}$ = +0.007 ppm change/month; s_m = 0.070 ppm change/month; s_{yp} = 0.53																		

[a] T = Time in months since the initial analysis

[b] See Table 3

TABLE 7. STABILITY DATA FOR SO_2/NITROGEN IN ALUMINUM CYLINDERS
(cont'd)

ANALYSIS NO.	INITIAL ANALYSIS			SUBSEQUENT ANALYSIS[a]														
Cylinder No.	Date	Conc. (ppm)	Source[b]	T	ppm	T	ppm	T	ppm	T	ppm	T	ppm	T	ppm		m	b	s_y
CAL916-245	08-01-81	78.4	D	11	79.3												+0.082	78.40	0.64
SP10745-254	10-01-80	85.0	E	24	83.4												-0.067	85.00	1.13
LL9353-270	09-01-80	87.1	A	3	84.9	10	88.0	21	87.3	27	87.0	33	87.0				+0.023	86.52	1.04
CAL7749-251	07-01-81	87.3	D	1	86.9	23	89.2										+0.093	87.06	1.23
FF7351-249	11-01-80	91.5	A	4	87.4	8	83.5	10	84.4	11	82.8	17	85.5	24	82.4		-0.294	88.47	3.20
CAL537-280	03-01-82	90.5	B	7	89.2	14	90.4										-0.007	90.08	0.72
FF9465-278	01-01-81	92.5	B	10	89.6	15	88.9	21	88.4	26	88.5						-0.155	91.81	1.70
CC5764-256	02-25-81	93.5	A	12	95.3	24	93.1										-0.017	94.17	1.17
JJ1835-271	03-01-81	94.5	A	2	94.9	22	94.7										+0.006	94.65	0.20
FF9467-277	10-01-80	94.4	B	11	94.1												-0.027	94.40	0.21
FF7267-257	12-02-81	95.6	C	6	97.8	14	97.0										+0.089	96.21	1.11
LL10224-275	11-01-81	96.1	B	5	95.8	10	95.8										-0.030	96.05	0.17
FF6309-276	02-01-80	96.4	B	7	102.0	25	94.5										-0.144	99.17	3.90
FF3790-279	07-01-81	98.5	B	5	98.5	11	99.4	16	98.7	23	98.5						+0.003	98.69	0.39
FF14630-258	12-03-81	98.7	C	7	99.6	14	99.7										+0.071	98.83	0.55
BAL396-285	03-01-79	98.8	D	11	98.7	22	99.3										+0.023	98.68	0.32
BAL1178-282	04-01-80	98.9	D	8	99.7	28	98.6	38	98.1								-0.029	99.36	0.67
CC14309-255	08-27-81	99.4	B	12	100.4												+0.083	99.40	0.71
BAL546-304	12-01-81	100.3	D	5	99.4	10	99.5	13	99.3								-0.067	100.10	0.46
FF1926-303	12-01-81	100.4	C	5	103.2	12	103.0										+0.201	101.06	1.56
FF14311-301	11-01-81	100.5	B	9	100.5	17	100.7	19	100.0								-0.012	100.56	0.30
FF1822-300	06-01-80	101.1	B	8	97.8	17	94.9	25	95.1								-0.249	100.34	2.90
FF9445-299	12-01-80	101.3	B	11	99.8	20	98.3	23	99.3								-0.108	101.14	1.25
FF9440-295	11-01-80	101.6	B	12	104.7	14	100.7	19	98.3	24	98.7						-0.162	103.03	2.58
FF1725-296	06-01-80	101.7	B	6	98.3	8	98.3	9	98.8	17	97.1						-0.250	100.84	1.72
FF9526-297	11-01-80	102.3	B	4	101.8	13	100.9										-0.106	102.27	0.71
FF8774-298	02-01-80	102.3	B	5	104.1	12	101.1	22	101.0								-0.100	103.10	1.44
FF2230-302	03-01-80	102.8	B	4	102.1	18	98.5	23	98.4	27	98.4						-0.181	102.64	2.21
FF5530-286	06-01-80	104.4	B	11	101.6	21	100.8	30	100.3								-0.133	103.84	1.83
LL4056-288	10-01-80	109.0	A	16	109.0	23	110.0										+0.036	108.87	0.58
LL9857-289	10-01-80	109.0	A	9	111.0	25	111.0										+0.071	109.53	1.16
LL3943-290	10-01-80	109.0	A	8	109.0	25	108.0										-0.043	109.14	0.58
LL9635-287	10-01-80	110.0	A	16	110.0	29	113.0										+0.100	109.51	1.73

Summary Statistics: $\bar{m}$ = -0.039 ppm change/month; s_m = 0.115 ppm change/month; s_{yp} = 1.69

[a] T = Time in months since the initial analysis

[b] See Table 3

TABLE 7. STABILITY DATA FOR SO_2/NITROGEN IN ALUMINUM CYLINDERS
(cont'd)

ANALYSIS NO.	INITIAL ANALYSIS			SUBSEQUENT ANALYSIS[a]													
Cylinder No.	Date	Conc. (ppm)	Source[b]	T	ppm	T	ppm	T	ppm	T	ppm	T	ppm	T	ppm	m	b	s_y
FF1084-291	03-01-81	153.0	A	8	155.0	18	152.0									-0.066	153.90	1.53
LL315-294	10-01-80	189.0	A	17	192.0	25	193.0									+0.163	189.06	2.08
LL4245-293	06-01-81	197.0	A	12	205.0	17	199.0									+0.218	198.22	4.16
LL3651-292	10-01-80	199.0	A	4	204.0	16	201.0									+0.038	201.08	2.52
FF6418	03-01-81	234.0	A	8	232.0	20	234.0									+0.013	233.21	1.16
FF5335	08-01-79	243.0	A	7	250.0	27	250.0									+0.202	245.38	4.04
FF6455	06-01-79	234.0	A	9	234.0	27	232.0									-0.079	234.29	1.16
FF1188	03-01-81	375.0	A	8	375.0	18	376.0									+0.057	374.84	0.58
FF1101	06-01-79	378.0	A	9	378.0	27	379.0									+0.040	377.86	0.58
FF1173	07-01-79	375.0	A	20	376.0	38	376.0									+0.027	375.15	0.58

Summary Statistics: $\bar{m}$ = +0.061 ppm change/month; s_m = 0.103 ppm change/month; s_{yp} = 2.24

[a] T = Time in months since the initial analysis

[b] See Table 3

versus time in months since the initial analysis and the standard deviation (s_y) of the y-axis values (sulfur dioxide concentrations). The data were subdivided into concentration ranges and analyzed according to a median concentration. The concentration ranges were selected according to what appeared to be natural gaps in the concentration distribution of the data. Also, the use of relatively small concentration intervals allows one to assume equal variances in the analysis. These data were divided into four concentration ranges, 8 to 22, 45 to 56, 78 to 110 and 152 to 375 ppm.

Concentration Range 9 to 22 ppm--

For SO_2/nitrogen in aluminum cylinders, 9 to 22 ppm, there were 10 cylinders with measured concentrations ranging from 9.3 to 21.5 ppm (see Table 7). One of the cylinders was analyzed twice over eleven months and the remaining nine cylinders were analyzed three times each over time periods ranging from 13 to 26 months.

The 10 calculated regression equation slopes include four negative, five positive and one zero value. The average slope was $\bar{m}$ = -0.003 ppm change/month and the standard deviation of the slopes about that average was s_m = 0.020 ppm change/month (see summary statistics in Table 7). Using the Student's t-test to test the hypothesis that the true mean slope was zero yielded;

$$t = \frac{\bar{m} - 0}{s_m/\sqrt{k}} = \frac{-0.003 - 0}{0.020/\sqrt{10}} = 0.904$$

Comparing the calculated t value to tabulated values for 10 degrees of freedom indicate that average slopes of -0.003 ppm change/month or larger can be expected to occur more than 35 percent of the time due to chance causes alone. Thus, there was no reason to reject the hypothesis that the true mean slope was zero. An approximate 95 percent probability interval for slopes in this category was $\bar{m} \pm 2\ s_m$ = -0.003 $\pm$ 0.040 ppm change/month. For an 18 month period, for example, the 95 percent probability interval for total change in concentration based on the distribution of the slopes was -0.054 $\pm$ 0.720 ppm (-0.774 to +0.666 ppm) and for a median concentration value of 15 ppm the interval expressed as a percent was -5.2 percent to +4.4 percent.

The precision of analysis as estimated by the pooled standard deviation of the measured concentrations was s_{yp} = 0.15 ppm (see Table 7). The approximate 95 percent probability interval for the uncertainty (excluding bias) of a SO_2/nitrogen concentration estimated by one analysis was $\pm 2\ s_{yp}$ = 0.30 ppm or $\pm$2.0 percent at a concentration of 15 ppm.

Based on the above results for the average slope it was concluded that SO_2/nitrogen in aluminum cylinders at concentrations between 9 and 22 ppm is stable for periods of up to 18 months and that the precision of analysis indicates that repeated Protocol No. 2 analyses over that time period are not necessary.

Concentration Range 45 to 56 ppm--

For SO_2/nitrogen in aluminum cylinders, 45 to 56 ppm, there were 21 cylinders with measured concentrations ranging from 44.8 to 56.4 ppm (see Table 7). Five or the cylinders were analyzed three times over time periods ranging from 11 to 35 months, the remaining 16 cylinders were analyzed twice over time periods ranging from 11 to 26 months.

The 21 calculated regression equation slopes include nine negative, eleven positive, and one zero value. The average slope was $\bar{m}$ = +0.007 ppm change/month and the standard deviation of the slopes about that average was s_m = 0.070 ppm change/month (see summary statistics in Table 7). Using the Student's t-test to test the hypothesis that the true mean slope was zero yielded:

$$t = \frac{\bar{m} - 0}{s_m/\sqrt{k}} = \frac{+0.007 - 0}{0.070/\sqrt{21}} = 0.458$$

Comparing the calculated t value to tabulated values for 20 degrees of freedom indicate that the average slopes of 0.007 ppm change/month or larger can be expected to occur more than 50 percent of the time due to chance causes alone. Thus, there was no reason to reject the hypothesis that the true mean slope was zero. An approximate 95 percent probability interval for slopes in this category was $\bar{m} \pm 2\ s_m$ = +0.007 $\pm$ 0.140 ppm change/month. For an 18 month period, for example, the 95 percent probability interval for total change in concentration based on the distributation of the slopes was +0.126 $\pm$ 2.510 ppm

(-2.394 to 2.646 ppm) and for a median concentration value of 51 ppm the interval expressed as a percent was -4.7 percent to +5.2 percent.

The precision of analysis as estimated by the pooled standard deviation of the measured concentrations was s_{yp} = 0.53 ppm (see Table 7). The approximate 95 percent probability interval for the uncertainty (excluding bias) of a SO_2/nitrogen concentration estimated by one analysis is $\pm 2\ s_{yp}$ = 1.06 ppm or $\pm$ 2.1 percent at a median concentration of 51 ppm.

Based on the above results for the average slope it was concluded that SO_2/nitrogen in aluminum cylinders at concentrations between 45 and 56 ppm is stable for periods of up to 18 months and that the precision of analysis indicates that repeated Protocol No. 2 analyses over that time period are not necessary.

Concentration Range 78 to 110 ppm--

For SO_2/nitrogen in aluminum cylinders, 78 to 110 ppm, there were 33 cylinders with measured concentrations ranging from 78.4 to 113.0 ppm (see Table 7). One of the cylinders was analyzed seven times over 24 months, another cylinder was analyzed six times over 33 months, five of the cylinders were analyzed five times over time periods ranging from 17 to 27 months, seven of the cylinders were analyzed four times over time periods ranging from 13 to 38 months, fifteen of the cylinders were analyzed three times over time periods ranging from 10 to 29 months, and the remaining four cylinders were analyzed twice over time periods ranging from 11 to 24 months.

The 33 calculated regression equation slopes include twenty negative and thirteen positive values. The average slope was $\bar{m}$ = -0.039 ppm change/month and the standard deviation of the slopes about that average was s_m = 0.115 ppm change/month (see summary statistics in Table 7). Using the Student's t-test to test the hypothesis that the true mean slope was zero yielded:

$$t = \frac{\bar{m} - 0}{s_m/\sqrt{k}} = \frac{-0.039 - 0}{0.115/\sqrt{33}} = 1.948$$

Comparing the calculated t values to tabulated values for 32 degrees of freedom indicates that average slopes of 0.039 ppm change/month or

larger can be expected to occur approximately 7 percent of the time due to chance causes alone. Thus, there was no reason to reject the hypothesis that the true mean slope was zero. An approximate 95 percent probability intervals for slopes in this category was $\bar{m} \pm 2$ s_m = -0.039 $\pm$ 0.230 ppm change/month. For an 18 month period, for example, the 95 percent probability interval for total change in concentration based on the distribution of the slopes was -0.702 $\pm$ 4.14 ppm (-4.842 to 3.438 ppm) and for a median concentration value of 94 ppm the interval expressed as a percent was -5.2 percent to +3.7 percent.

The precision of analysis as estimated by the pooled standard deviation of the measured concentration was s_{yp} = 1.69 ppm (see Table 7). The approximate 95 percent probability interval for the uncertainty (excluding bias) of a SO_2/nitrogen concentration estimated by one analysis was $\pm$ 2 s_{yp} = 3.38 ppm or $\pm$ 3.6 percent at a concentration of 94 ppm.

Based on the above results for the average slope it was concluded that SO_2/nitrogen in aluminum cylinders at concentrations between 78 and 110 ppm is stable for time periods greater than 18 months and that the precision of analysis indicates that repeated Protocol No. 2 analyses during that time interval are not necessary.

Concentration Range 152 to 375 ppm--

For SO_2/nitrogen in aluminum cylinders, 152 to 375 ppm, there were 10 cylinders with measured concentrations ranging from 152 to 376 ppm (see Table 7). All of the cylinders were analyzed three times over time periods ranging from 16 to 38 months.

The 10 calculated regression equation slopes include two negative, and eight positive values. The average slope was $\bar{m}$ = +0.061 ppm change/month and the standard deviation of the slopes about that average was s_m = 0.103 ppm change/month (see summary statistics Table 7). Using the Student's t-test to test the hypothesis that the true mean slope was zero yielded:

$$t = \frac{\bar{m} - 0}{s_m/\sqrt{k}} = \frac{+0.061 - 0}{0.103/\sqrt{10}} = 1.873$$

Comparing the calculated t value to tabulated values for 9 degrees of freedom indicates that average slopes of 0.061 ppm change/month or larger can be expected to occur more than 7 percent of the time due to chance causes alone. Thus, there was no reason to reject the hypothesis that the true mean slope was zero. An approximate 95 percent probability interval for slopes in this category was $\bar{m} \pm 2\ s_m$ = +0.061 $\pm$ 0.206 ppm change/month. For an 18 month period, for example, the 95 percent probability interval for total change in concentration based on the distribution of the slopes was 1.098 $\pm$ 3.708 ppm (-2.610 to 4.806 ppm) and for a median concentration value of 264 ppm the interval expressed as a percent is -1.0 percent to +1.8 percent.

The precision of analysis as estimated by the pooled standard deviation of the measured concentrations is s_{yp} = 2.24 ppm (see Table 7). The approximate 95 percent probability interval for the uncertainty (excluding bias) of a SO_2/nitrogen concentration estimated by one analysis is $\pm 2\ s_{yp}$ = 4.48 ppm, or $\pm$ 1.7 percent at a median concentration of 264 ppm.

Based on the above results for the average slope it was concluded that SO_2/nitrogen in aluminum cylinders at concentrations between 152 and 375 ppm is stable for time periods greater than 18 months and that the precision of analysis indicates that repeated Protocol No. 2 analyses over that time interval are not necessary.

Carbon Monoxide In Air Contained In Steel Cylinders

Stability data from five steel cylinders containing carbon monoxide with a balance gas of air were analyzed. This stability data, cylinder number, date of initial analysis, initial concentration, method of initial analysis, time (T) in months since the initial analysis and the analyzed concentration in ppm are contained in Table 8. Also contained in this table are the linear regression constants, slope (m) and intercept (b), calculated from the analyzed concentrations versus months since the initial analysis and the standard deviation of the y-axis values (carbon monoxide concentrations). These data were analyzed as one concentration range, 9 to 11 ppm.

TABLE 8. STABILITY DATA FOR CO CONTAINED IN STEEL CYLINDERS

ANALYSIS NO.	INITIAL ANALYSIS			SUBSEQUENT ANALYSIS[a]																	
Cylinder No.	Date	Conc. (ppm)	Source[b]	T	ppm	T	ppm	T	ppm	T	ppm	T	ppm	T	ppm	T	ppm	m	b	s_y
CO/Air																					
58	07-08-80	9.5	C	29	9.0																
56	07-08-80	9.7	C	25	9.5	28	9.2														
G016194	06-01-82	10.0	A	11	9.9																
50	11-17-80	10.6	C	34	9.0																
53	11-17-80	10.7	C	34	8.9																
																		-0.017	9.50	0.35	
																		-0.014	9.72	0.25	
																		-0.009	10.00	0.07	
																		-0.047	10.60	1.13	
																		-0.053	10.70	1.27	
Summary Statistics: $\bar{m}$ = -0.028 ppm change/month; s_m = 0.020 ppm change/month; s_{yp} = 0.72																					
CO/N_2																					
SG16465C-50	09-30-81	18.6	C	3	18.3	6	18.2	9	18.3	12	18.0	14	17.7	18	17.9			-0.042	18.51	0.30	
SG13547-52	09-23-81	19.5	C	2	19.9	6	19.8	8	20.0	11	19.9	13	19.8	18	19.5	20	19.8	-0.002	19.79	0.18	
SG17932C-51	09-10-81	21.0	C	3	20.5	5	20.5	8	20.6	11	20.5	14	20.3					-0.035	20.81	0.23	
SG11318C	09-23-81	32.6	C	2	32.9	6	32.8	8	32.7	11	32.8	13	32.9	18	32.6	20	33.0	+0.006	32.73	0.15	
SG6734C	09-10-81	32.9	C	3	32.5	5	32.6	8	32.5	11	32.4	14	32.6					-0.019	32.72	0.17	
SG15483C	09-30-82	33.2	C	3	32.6	5	32.5	8	32.8	12	32.5	14	32.6	18	31.7			-0.055	33.03	0.45	
SG6906C	09-30-81	37.2	C	3	36.5	5	36.4	8	36.5	12	36.2	14	35.7	18	35.5			-0.083	36.99	0.56	
SG7059	09-10-81	40.0	C	3	39.4	5	39.6	8	39.5	11	39.4	14	39.5					-0.027	39.75	0.23	
SG13142C	09-01-81	42.7	C	3	42.1	5	43.0	8	42.0	11	42.1	14	42.2					-0.038	42.61	0.40	
Summary Statistics: $\bar{m}$ = -0.032 ppm change/month; s_m = 0.029 ppm change/month; s_{yp} = 0.33																					
T741532	03-25-81	1000.0	C	9	999.6	16	997.2	23	995.1									-0.220	1000.62	2.28	
T744682	03-25-81	1000.0	C	9	1000.9	16	1000.5	23	997.8									-0.086	1000.83	1.38	
Summary Statistics: $\bar{m}$ = -0.153 ppm change/month; s_m = 0.095 ppm change/month; s_{yp} = 1.88																					

[a] T = Time in months since the initial analysis

[b] See Table 3

For CO/air in steel cylinders, 9 to 11 ppm, there were 5 cylinders with measured concentrations ranging from 9 to 11 ppm (see Table 8). One of the cylinders was analyzed three times over 28 months, four of the cylinders were analyzed twice each over time periods ranging from 11 to 34 months.

The five calculated regression equation slopes were all negative values. The average slope was $\bar{m} = -0.028$ ppm change/month and the standard deviation of the slopes about that average was $s_m = 0.020$ ppm change/month (see summary statistics in Table 8). Using the Student's t-test to test the hypothesis that the true mean slope was zero yielded:

$$t = \frac{\bar{m} - 0}{s_m/\sqrt{k}} = \frac{-0.028 - 0}{0.020/\sqrt{5}} = 3.13$$

Comparing the calculated t value to tabulated values for 4 degrees of freedom indicate that average slopes as large as 0.028 ppm change/month or larger will, on the average, occur no more than 5 percent of the time due to chance causes alone. Thus, there was reason to reject the hypothesis that the true mean slope was zero. An approximate 95 percent probability interval for slopes in this category was $\bar{m} \pm 2 s_m = -0.028 \pm 0.040$ ppm change/month. For an 18 month period, for example, the 95 percent probability interval for total change in concentration based on the distribution of the slopes was -0.504 ± 0.729 ppm (-1.224 to +0.216 ppm) and for a median concentration value of 10 ppm the interval expressed as a percent was -12.2 percent to -2.2 percent.

Based on the above results for the average slope it was concluded that the stability of CO/air in steel cylinders at concentrations around 10 ppm is such that the present recertification period of 6 months should not be changed.

Carbon Monoxide In Nitrogen Contained In Steel Cylinders

Stability data from 11 steel cylinders containing carbon monoxide with a balance gas of nitrogen were analyzed. This stability data,

cylinder number, date of initial analysis, initial concentration, method of initial analysis, time (T) in months since the initial analysis and the analyzed concentration in ppm are contained in Table 8. Also contained in this table are the linear regression constants, slope (m) and intercept (b), calculated from analyzed concentrations versus months since the initial analysis and the standard deviation (s_y) of the y-axis values (carbon monoxide concentrations). The data were grouped and analyzed according to concentration. The concentration ranges were based on the concentration distribution of the data. These data were divided into two concentration ranges, 19 to 43 ppm and 1000 ppm.

Concentration Range 19 to 43 ppm--

For CO/nitrogen in steel cylinders 19 to 43 ppm, there were 9 cylinders with measured concentrations ranging from 18.2 to 43 ppm (see Table 8). Two of the cylinders were analyzed eight times over a time period of 20 months, three of the cylinders were analyzed seven times over an 18 month time period and the remaining four cylinders were analyzed six times over a 14 month time period.

The 9 calculated regression equation slopes include eight negative and one positive value. The average slope was $\bar{m} = -0.032$ ppm change/month and the standard deviation of the slopes about that average was $s_m = 0.029$ ppm change/month (see summary statistics in Table 8). Using the Student's t-test to test the hypothesis that the true mean slope was zero yielded:

$$t = \frac{\bar{m} - 0}{s_m/\sqrt{k}} = \frac{-0.032 - 0}{0.029/\sqrt{9}} = 3.310$$

Comparing the calculated t value to tabulated values for 8 degrees of freedom indicates that average slopes as large as 0.032 ppm change/month will occur no more than 1 percent of the time due to chance causes alone. Thus, there was reason to reject the hypothesis that the true mean slope was zero. An approximate 95 percent probability interval for slopes in this category is $\bar{m} \pm 2\ s_m = -0.032 \pm 0.058$ ppm change/month. For an 18 month period, for example, the 95 percent

probability interval for total change in concentration based on the distribution of the slopes was -0.576 ± 1.044 ppm (-1.62 to +0.468 ppm) and for a median concentration value of 31 ppm the interval expressed as a percent was -5.2 percent to +1.5 percent.

The precision of analysis as estimated by the pooled standard deviation of the measured concentrations was s_{yp} = 0.33 ppm (see Table 8). The approximate 95 percent probability interval for the uncertainty (excluding bias) of a CO/nitrogen concentration estimated by one analysis was ± 2 s_{yp} = 0.66 ppm or ± 2.1 percent at a concentration of 31 ppm.

The above results for the distribution of slopes indicate that to ensure that uncertainties in concentration due to changes in time do not exceed 2 percent (with approximately 95 percent confidence) the present recertification requirement of reanalysis every 6 months should not be changed.

Concentration 1000 ppm--

For CO/nitrogen in steel cylinders, at 1000 ppm, there were 2 cylinders. Both of the cylinders were analyzed four times each over 23 months.

The two calculated regression equation slopes were both negative. The average slope was $\bar{m}$ = -0.153 ppm change/month and the standard deviation of the slopes about that average was s_m = 0.095 ppm change/month (see summary statistics in Table 8). Using the Student's t-test to test the hypothesis that the true mean slope was zero yielded:

$$t = \frac{\bar{m} - 0}{s_m/\sqrt{k}} = \frac{-0.153 - 0}{0.095/\sqrt{2}} = 2.278$$

Comparing the calculated t value to tabulated values for 1 degree of freedom indicate that average slopes of 0.153 ppm change/month or larger can be expected to occur more than 20 percent of the time due to chance causes alone. Thus, there was no reason to reject the hypothesis that the true mean slope was zero.

The precision of analysis as estimated by the pooled standard deviation of the measured concentrations was s_{yp} = 9.88 ppm (see

Table 8). The approximate 95 percent probability interval for the uncertainty (excluding bias) of a CO/nitrogen concentration estimated by one analysis was $\pm$ 2 s_{yp} = 3.76 ppm or $\pm$ 0.4 percent at a concentration of 1000 ppm.

The data set of two cylinders is too small by itself to reach a conclusion on stability. However, due to the indicated instability of the nine cylinders at concentrations between 19 and 43 ppm it would seem reasonable at this time to retain the present recertification requirements of reanalysis every 6 months for all CO in steel cylinders.

DISCUSSION

For reactive gases in aluminum cylinders the worst case average percent change ($\bar{P}$), based on the average slope ($\bar{m}$), over a 24 month period was -1.4 percent (see Table 1, Section 1, of this report) for CO/Air contained in aluminum cylinders at concentrations between 5 and 11 ppm. However, this category showed an average change of 1 percent for an eighteen month period. All of the remaining pollutant categories contained in aluminum cylinders showed average changes of less than one percent over an eighteen month period. For this reason, an eighteen month recertification time period is being recommended for reactive gases contained in aluminum cylinders. The average percent change and the 95 percent probability interval of the percent change for reactive gases contained in aluminum cylinders for an eighteen month period have been summarized in Table 9.

The worst case average percent change over a 24 month period was -6.7 percent (see Table 2, Section 1, of this report) for CO/Air contained in steel cylinders at concentrations between 9 and 11 ppm, and this same category showed an average change of -1.7 percent change for a six month period. For this reason it is recommended that the six month recertification period remain unchanged for CO/air in steel cylinders at concentrations around 10 ppm.

The average percent change for CO/N_2 gases contained in steel cylinders at concentrations between 19 and 43 ppm is less than 1 percent for the 6 month period only. Thus, it is recommended that the 6 month recertification period remain unchanged for CO/N_2 in steel cylinders.

TABLE 9. AVERAGE PERCENT CHANGE AND PROBABILITY LIMITS OF REACTIVE GASES CONTAINED IN ALUMINUM CYLINDERS FOR EIGHTEEN MONTHS

Pollutant/Balance Gas	Concentration Range (ppm)	Concentration Median (ppm)	$\bar{P} \pm 2\ s_p$[a] (Percent)
CO/Air	5 to 11	7	-1.0 ± 6.6
CO/Air	17 to 45	30	0.0 ± 2.0
CO/N_2	5 to 15	10	$+0.2 \pm 3.6$
CO/N_2	14 to 46	30	$+0.4 \pm 2.2$
CO/N_2	100 to 1000	500	$+0.4 \pm 2.0$
CO/N_2	2500 to 5000	3750	-0.0 ± 4.8
NO/N_2	10 to 22	16	0.3 ± 3.2
NO/N_2	43 to 55	49	-0.9 ± 5.2
NO/N_2	80 to 113	97	-0.2 ± 4.2
SO_2/N_2	9 to 22	15	-0.4 ± 5.0
SO_2/N_2	45 to 56	51	-0.2 ± 5.0
SO_2/N_2	78 to 110	94	$+0.7 \pm 4.4$
SO_2/N_2	152 to 375	264	-0.4 ± 1.4

[a] $\bar{P}$ = Average percent change at the nominal concentration over a specified time period, percent

s_p = Standard deviation of the percent change at the nominal concentration over the time period, percent

TABLE 10. PERCENT CHANGE AND PROBABILITY LIMITS OF REACTIVE GASES CONTAINED IN STEEL CYLINDERS FOR EIGHTEEN MONTHS

Pollutant/Balance Gas	Concentration Range (ppm)	Concentration Median (ppm)	$\bar{P} \pm 2\ s_p$ (Percent)
CO/Air	9 to 11	10	-5.0 ± 7.2
CO/N_2	10 to 43	31	-1.9 ± 3.4
CO/N_2	1000	1000	-0.3 ± 0.4

The average percent change and the 95 percent probability limits for the percent change for CO/nitrogen gases contained in steel cylinders for an 18 month period have been calculated in Table 10. These data indicate that CO/nitrogen in steel cyinders is not as stable as CO/nitrogen in aluminum cylinders for an 18 month period.

SECTION 5

CONCLUSIONS AND RECOMMENDATIONS

The data contained in this report, indicates that reactive gases (CO/Air, CO/N_2, NO/N_2, SO_2/N_2) contained in aluminum cylinders, will remain stable for at least eighteen months. However, it is desirable that a pollutant gas being used as a calibration or audit standard be analyzed at least twice within its useful lifetime. A pollutant gas user should take into account the consumption rate of the gas and plan for a second analysis before the cylinder is empty. This second analysis will verify the first analysis and assist the quality assurance coordinator in data validation.

It is recommended that the present requirement for reanalysis of reactive gases every six months be extended to eighteen months for the following:

- Carbon monoxide in air in aluminum cylinders at concentrations between 5 ppm and 45 ppm. NOTE: To ensure uncertainties of less than 10 percent in measured concentrations near 5 ppm, it may be necessary to use the average of two Protocol No. 2 analyses.

- Carbon monoxide in nitrogen in aluminum cylinders at concentrations between 5 ppm and 5,000 ppm. NOTE: To ensure uncertainties of less than 10 percent in measured concentrations near 5 ppm, it may be necessary to use the average of two Protocol No. 2 analyses.

- Nitric oxide in nitrogen in aluminum cylinders at concentrations between 10 ppm and 150 ppm.

- Sulfur dioxide in nitrogen in aluminum cylinders at concentrations between 9 ppm and 375 ppm.

The data contained in this report, indicates that CO/Air and CO/N_2 contained in steel cylinders will remain stable for no more than six months. However, this conclusion was based upon a relatively small data set. Based upon results from this small data set and the indicated instability, it is recommended that the present requirement for reanalysis every six months remain unchanged for the following:

- Carbon monoxide in air contained in steel cylinders.
- Carbon monoxide in nitrogen contained in steel cylinders.

Current recertification requirements should remain unchanged for reactive gases and cylinder types not considered in this report.

SECTION 6

REFERENCES

1. Quality Assurance Handbook for Air Pollution Measurement Systems, Ambient Air Specific Methods, Volume II, Section 2.0.7, EPA-600/4-77-027a, May 1977.

2. Code of Federal Regulations, Title 40, Part 58, Appendix A (Quality Assurance Requirements for State and Local Air Monitoring Stations (SLAMS) as amended January 20, 1983 (48 FR 2528-2530).